Title: **Water-gas Shift with Integrated Hydrogen Separation Process**

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Abstract

In recent years, there has been renewed interest in the water-gas shift reaction because of its potential use in conjunction with fuel-cell power generation, an attractive, energy-efficient process currently undergoing rapid development for both power plant and transportation applications. Optimization of the WGS system for hydrogen production for fuel cells is of particular interest to the energy industry. To this end, it is desirable to couple the WGS reaction to hydrogen separation using a semi-permeable membrane, with both processes carried out at high temperature and pressure to improve reaction kinetics. Reduced equilibrium conversion of the WGS reaction at high temperatures is overcome by product H_2 removal via the membrane.

This project involves fundamental research and development of novel cerium oxide-based catalysts for the water-gas-shift reaction and the integration of these catalysts with H_2 -separation membranes supplying high purity hydrogen for fuel cell power generation. Conditions matching the requirements of coal gasifier-exit gas streams will be examined in the project.

The approach taken in this work is to treat the WGS catalyst and membrane as a single, tightly coupled system designed to operate efficiently over a wide temperature window. This is possible when a hydrogen-selective membrane of high permeance is juxtaposed to a highly active catalyst that, accordingly, maintains a substantial driving force for H_2 permeation. Novel WGS catalysts and thin Pd-alloy H_2-selective membranes, each independently under investigation in the laboratories of the co-PIs, will be further developed and integrated as a system in this project.

An active and robust catalyst, currently under development at Tufts comprises doped cerium oxide (ceria) as the backbone and copper oxide as the minor component, the two working cooperatively over the temperature range of 150-650 ^oC. An important feature of ceria-based catalysts is that, unlike Cu-ZnO-Al_2O_3, they do not lose their activity at temperatures > 250^oC. Thus, these novel catalysts can replace both low- and high-temperature shift catalysts**.** In this

project, we will compare the activity of Cu- ceria and also FeO_x- ceria to commercial catalysts, especially the high-temperature shift catalysts based on iron oxide.

In parallel research at Tufts, a membrane system based on a 25-µm foil of a Pd alloy, has been undergoing development for the separation of H_2 from a variety of gas mixtures. This has been continuously operated for several thousand hours in the temperature range 300-400ºC, yielding >99.999% H_2. Furthermore, we have obtained very thin (3-8 µm thick), unsupported Pd-alloy membranes with correspondingly elevated hydrogen permeances. An optimized WGS catalyst coupled with such an H_2-selective membrane offers the most attractive solution for rapid development of coal gas-based fuel cell technology**.**

In initial work this first year, we have prepared a series of nanostructured Cu- and Fe-containing ceria catalysts by a special gelation/precipitation technique followed by air calcination at 650^{o}C. Each sample was characterized by ICP for elemental composition analysis, BET-N2 desorption for surface area measurement, and by temperature-programmed reduction to evaluate the catalyst reducibility. Screening tests in a flow microreactor are currently underway. The plan of future work includes continued catalyst synthesis and characterization, kinetic and parametric studies and catalyst structural evaluation under practical WGS conditions. In parallel, H_2 fluxes and purity will be monitored in permeation experiments carried out under the same conditions, using Pd-alloy membranes with a range of thicknesses. Based on these studies, a working model of the operation of an integrated membrane reactor will be developed, and initially employed to facilitate design of a prototype system. The focus will be upon matching catalyst activity and membrane permeance. Once the prototype is fabricated, an extended series of experiments will be undertaken with the aim of validating and, as necessary, modifying the theoretical model.

List of Publications, Presentations, and Students Supported by the Grant

- Q. Fu, S. Kudriavtseva, H. Saltsburg, M. Flytzani-Stephanopoulos, "High-stability water-gas shift catalysts based on nanocrystalline ceria", paper presented at the 221st National ACS meeting in San Diego, CA, April 1-5, 2001.
- Q. Fu, X. Qi, S. Kudriavtseva, H. Saltsburg, M. Flytzani-Stephanopoulos, "Oxygen storage capacity of metal-modified cerium oxide", in preparation.

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